

Electroactive Gate Materials for a Hydrogen Peroxide Sensitive ^EMOSFET

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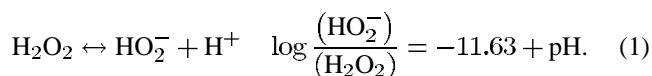
Abstract—This paper describes the detection principle of a hydrogen peroxide sensor based on the electrolyte metal oxide semiconductor field effect transistor (^EMOSFET) and possibilities of using different types of redox materials as the gate material for the sensor with respect to the sensitivity and detection limit. After discussing the fundamentals of hydrogen peroxide detection and a short description of the ^EMOSFET characteristics in terms of its threshold voltage, the basic measuring principle of hydrogen peroxide using the ^EMOSFET is shown. The ^EMOSFET with electro-active gate materials such as iridium oxide, potassium ferric ferrocyanide, and Os polyvinylpyridine containing peroxidase, have been studied. These different materials are compared with each other with respect to their sensitivity, detection limit, and stability. The sensitivity of the sensors is improved by applying an external current between the gate and the solution.

Index Terms—^EMOSFET, hydrogen peroxide sensor, redox material.

I. INTRODUCTION

THE determination of trace amounts of hydrogen peroxide is of practical importance in medical, environmental, and biological fields. It is necessary to determine hydrogen peroxide, not only in chemical and industrial processes (for example, disinfection, waste-water treatment), but also as an intermediate product of an enzyme reaction in biochemical processes (for example, glucose determination). Therefore, a hydrogen peroxide sensor can be also used as an intermediate transducer for other biosensors. For this purpose, many types of hydrogen peroxide sensors have been developed.

The determination of hydrogen peroxide is based on its oxidizing or reducing properties. In aqueous solutions, the dissociation of hydrogen peroxide to HO_2^- and H^+ is represented by



Reduction or oxidation of hydrogen peroxide can take place at a noble metal electrode. Depending on the electrode potential, hydrogen peroxide can be reduced to water or oxidized to oxygen as illustrated in the corresponding Pourbaix diagram, shown in Fig. 1 [1]. The decomposition of hydrogen peroxide also depends largely on the surface conditions of the electrode.

In practice, depending on the concentration of hydrogen peroxide to be measured, there are many analytical methods

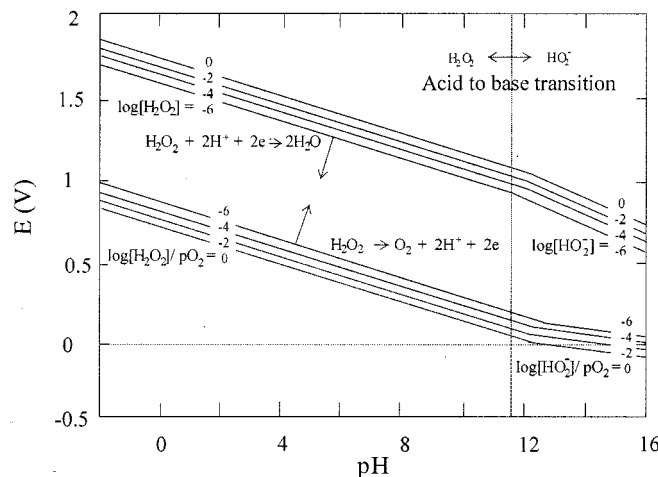


Fig. 1. Potential-pH equilibrium diagram of the system hydrogen peroxide-water, at 25 °C.

for assaying hydrogen peroxide, such as chemical and optical (spectrophotometric, fluorescent, and chemiluminescence) approaches. All methods mentioned above require complicated measurement set-ups, which are not suitable for a quick test in practical applications.

Another possibility of measuring hydrogen peroxide is by using an electrochemical sensor based on the reduction or oxidation at the working electrode (WE) of a sensor. In an amperometric sensor, these reactions occur at the working electrode, usually a Pt wire, by applying a suitable potential. To improve sensitivity and selectivity of the sensor, an enzyme can be immobilized on top of the electrode surface. One of the disadvantages of the amperometric sensors is the required high overpotential (~ 0.6 V) of hydrogen peroxide oxidation, which limits the selectivity of the sensor. This limitation can be prevented by using a redox mediator, which can mediate the oxidation of hydrogen peroxide. The currently preferred mediators are monomeric ferrocenes, quinones, and osmium bipyridine complexes. All have redox potentials of about 0.3–0.6 V positive with respect to the redox potential of the enzyme [2].

Another way to circumvent the selectivity problem encountered by amperometric hydrogen peroxide detection is by using a potentiometric sensor. The potentiometric sensor consists of a metallic wire and a specific electrode material on top of it. This electrode material should be electroactive with high catalytic properties for hydrogen peroxide. Fig. 2 shows the potential profile as a function of the position in an electrochemical cell, which consists of a Pt wire with a redox material on top of it as the sensing material, M , and a reference electrode, Ref, in the analyte solution, S . Note that all layers are conducting, thus not

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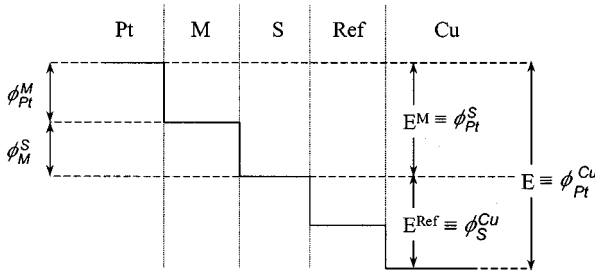


Fig. 2. Illustration of the potential as a function of position in the electrochemical cell, consisting of a Pt electrode with electroactive material M on top of it and a reference electrode, both in contact with solution S .

having a potential drop in the bulk, whereas potential profiles of double layers at the interfaces are neglected. The potential of the sensor electrode, E^M , is composed of two terms: ϕ_M^S and ϕ_{Pt}^M . The first term, ϕ_M^S , is generated by the exchange of counter ions which are present in the solution. This potential is usually called the Donnan potential. The second term, ϕ_{Pt}^M , is a contact potential, determined by the difference in the work function of electrons in the redox material and the platinum, respectively. In the conventional potentiometric hydrogen peroxide sensor, the electrode potential, which is generated by the redox reaction between the membrane material (M) and the hydrogen peroxide, is a function of the hydrogen peroxide concentration. This potential is measured with respect to a reference electrode, which introduces an additional potential E^{ref} . In this paper, it is shown that by using an ^EMOSFET, the same information about redox activity of hydrogen peroxide can be obtained by means of measuring a change in the threshold voltage of the MOSFET.

II. OPERATIONAL MECHANISM OF THE ^EMOSFET

Throughout the years, different FET-based sensors have been developed, such as the ISFET [3] and the ChemFET [4]. These sensors differ from the original electronic equivalent, the MOSFET, in the sense that the metal gate of the MOSFET is replaced by an electrolyte in which a reference electrode is placed. In fact, the metal wire of the reference electrode now acts as the gate of the device, which is usually connected to the ground lead of the amplifier to which the FET is connected. All interfacial potentials generated between this remote gate contact and the oxide of the FET are modulating the electric field in the gate oxide and thus the concentration of electrons in the channel region of the device. This action can be described in terms of the so-called threshold voltage, V_T , of the device. It means in practice that the value of V_T reflects, among others, the interfacial potential at the electrolyte/gate insulator, which is pH dependent in the case of the ISFET (bare oxide) or made pI dependent by adding a membrane which contains specific ionophores for the ions I , in case of the ChemFET. Of these types of sensors the working principle is simply the modulation of the charge on a capacitor, formed by the silicon-oxide-electrolyte system, by any potential source in the measurement chain formed by the silicon and the reference electrode. This concept does not differ from the original MOSFET's concept. Also, in this case, a certain threshold voltage, V_T , is defined, depending on a number of physical parameters such as fixed charge inside the oxide, the doping level of the silicon, and the

difference in work function of the gate material and the silicon. So, identical MOSFETs, one with an Al gate electrode and one with a Au gate electrode, have different values of the threshold voltage. This means that, in case the gate electrode consists of a material of which the work function can reversibly be modulated by a chemical reaction from outside, the FET will show a threshold voltage which is controlled by that chemical reaction. This gate material should be anyway an electronic conductor to make the device a MOSFET. The gate can be connected to the ground and the source and drain leads to a so-called source-drain follower. The source potential will then show the value of the threshold voltage of the device.

In practice, redox materials can be used as gate material. They can be deposited on top of the gate oxide in various ways. For the ground connection, a Pt layer is used beforehand, shaped around the gate area. So the gate material should be deposited over this Pt layer, including the gap, formed by the actual gate area. Fig.3(a) shows a cross section of the device and Fig. 3(b) shows the block diagram of the electronic circuit. Fig.4 shows the electrochemical representation of the system in terms of Fig. 2. It shows that the actual chain of measurement is from silicon to Pt (the platinum layer around the gate area) while the solution is not connected. This is the reason that the E of ^EMOSFET is set in upper case. It means that no reference electrode is placed in the solution and that ϕ_M^S is not influencing the measurement. The only variable in the chain of measurement is ϕ_{Pt}^M , the contact potential between the gate material and the platinum contact.

The electroactive gate material can take part in a redox reaction while exchanging ions or species of interest with the solution. The bulk of the gate material can be reversibly changed from the reduced to the oxidized state. Thus, the interfacial potential, ϕ_M^S , is changed depending on the reaction with the ions or the species to be exchanged and their concentration in the solution, but, as stated before, this effect is not measured. The contact potential, ϕ_{Pt}^M , is determined by the work function and thus by the ox/red ratio of the gate material only. The change in ϕ_{Pt}^M will be measured by means of a change in the threshold voltage of the ^EMOSFET:

$$\Delta V_T \equiv \Delta \phi_{Pt}^M = (2.3 RT/nF) \log[Ox]/[Red] \quad (2)$$

where R , F , and T have their usual meaning; n and $[Ox]/[Red]$ are the number of electrons involved in the redox reaction and ox/red ratio of the gate material, respectively.

The absolute value of the threshold voltage, V_T , contains several physical constants as in any conventional MOSFET, originating from the transistor processing, resulting in a certain bias value. In case the gate material is nearly completely oxidized or reduced, this situation can be chosen, together with the original bias, as a set point for any measurement. The measurement of V_T can then be interpreted as

$$V_T = (2.3 RT/nF) \log[Ox]/[Red]. \quad (3)$$

III. EXPERIMENTAL

A MOSFET-structure having a gate of 500 μm wide and 15 μm long was fabricated using standard NMOS processing

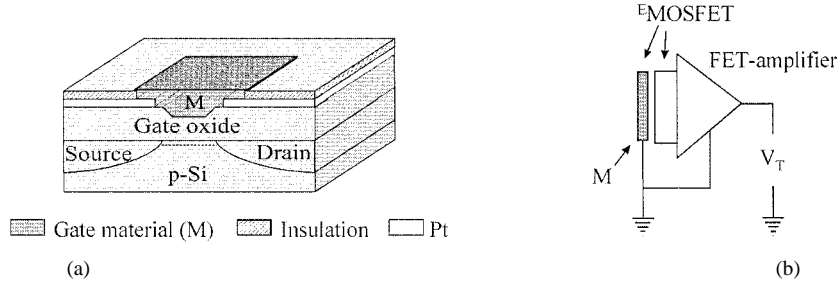


Fig. 3. (a) Schematic cross section of the E -MOSFET; (b) block diagram of the electronic system.

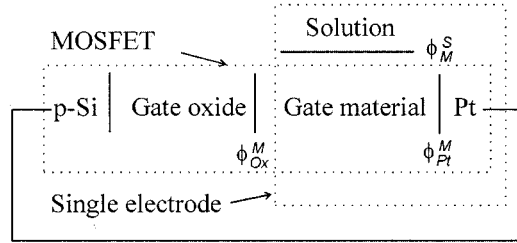


Fig. 4. Electrochemical system of the E -MOSFET.

steps without the usual aluminum gate [5]. Around the FET gate area, a Pt/Ti film, called a remote gate electrode, was deposited by sputtering. In order to insulate the relevant parts of the sensor from the solution, the sensor was packaged using Hysol[®] epoxy. To improve the adhesion of the epoxy to the chip, tantalum oxide and polyimide films were deposited beforehand on top of the sensor around the remote gate electrode. The tantalum oxide layer was obtained by reactive sputtering. The polyimide film was formed by spin coating.

Different types of the gate materials which have different catalytic properties for hydrogen peroxide, such as iridium oxide, potassium ferric ferrocyanide, which is usually called Prussian Blue (PB) and Os-polyvinylpyridine (Os PVP) containing horseradish peroxidase (HRP), have been deposited on the Pt electrode and gate area. The iridium oxide layer was deposited by sputtering. A Prussian Blue thin film was obtained by electrochemical deposition by applying a sweep voltage from 0.1 V to 0.5 V at sweep rate of 100 mV/s between the Pt remote gate electrode and a calomel electrode (SCE). The solution used for deposition of PB consists of 20 mM $K_3Fe(CN)_6$, 20 mM $FeCl_3$, and 0.01 M HCl [6]. The Os-polyvinylpyridine containing a horseradish peroxidase membrane, which is commercially available from BioAnalytical Systems, was deposited on top of the gate area by a coating technique. The hydrogen peroxide stock solutions were made from a 50% w/v solution of stabilized hydrogen peroxide.

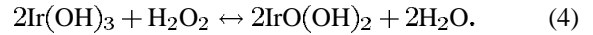
A specifically designed circuit as shown in Fig. 3(b) was used to determine changes in the threshold voltage of the E -MOSFET. The hydrogen peroxide sensitivity of the threshold voltage was determined in buffer solution made by dissolving analytical grade substances in demineralized water. The buffer solution contains 0.1M KCl as a supporting electrolyte. During all measurements, the solution was stirred at a constant rate while small known volumes of the hydrogen peroxide stock solution were added after every 5 min. Stable signals were

obtained within 15 s after adding the hydrogen peroxide stock solution.

IV. RESULTS AND DISCUSSION

A. H_2O_2 Sensor Based on Iridium Oxide

Earlier, an iridium oxide film has been investigated as the gate material, for making a hydrogen peroxide sensor [5]. The determination of hydrogen peroxide is based on the oxidation of the iridium oxide by hydrogen peroxide



In this case, (3) can be rewritten as

$$\begin{aligned} V_T &= \frac{2.3RT}{F} \log \frac{[IrO(OH)_2] \gamma_{IrO(OH)_2}}{[Ir(OH)_3] \gamma_{Ir(OH)_3}} \\ &= \frac{2.3RT}{2F} \log K_{IrOx} [H_2O_2] \end{aligned} \quad (5)$$

where γ is the activity coefficient, $[IrO(OH)_2]$ and $[Ir(OH)_3]$ are the concentrations of the oxidized and reduced iridium oxide, respectively, and K_{IrOx} is the equilibrium constant of reaction (4). The concentration of H_2O in the membrane is constant, thus it is not influencing the ox/red ratio of iridium oxide.

It is known that the exchange current I_o between iridium oxide and hydrogen peroxide is small because of the poor catalytic property of iridium oxide. Therefore, it takes quite a long time to reach the equilibrium state between the gate material and the solution. To accelerate this process, an additional external current is applied between the gate and the solution by applying a floating current source and a Pt counter electrode. This auxiliary (small) current will also reduce or oxidize the gate material, depending on its sign, in competition with the H_2O_2 effects. The value of V_T will not directly be influenced by this current, because there is no connection to the ground lead of the circuit of measurement as shown in Fig. 3(b).

From the theory of conventional electrode potentials, it is known that the difference in potential between the electrode potential when a current, I , is applied, $E^{M'}$, and the equilibrium potential E^M is usually called the overpotential, $\eta = E^{M'} - E^M$, given by the Butler Volmer equation

$$I = I_o \left(e^{-\alpha n \eta F / RT} - e^{(1-\alpha) n \eta F / RT} \right) \quad (6)$$

where I_o is the exchange current density between the gate material and the solution and α is the dimensionless transfer coef-

ficient of the reaction (4) ($0.1 < \alpha < 0.9$) [5]. For values of $\eta < RT/F$, (6) can be approximated by

$$\log \frac{I}{I_o} \approx -\frac{\alpha n \eta F}{2.3RT} \quad (7)$$

Because the redox electrode overpotential is not the result of a change in the interface potential (ϕ_M^S in Fig. 2 and 4) but due to changes in the bulk, it is concluded that the value of V_T will also change with η , resulting in

$$\begin{aligned} V_T &= \frac{2.3RT}{2F} \log K_{\text{IrOx}}[\text{H}_2\text{O}_2] - \frac{2.3RT}{F\alpha} \log \frac{I}{I_{\text{IrOx}}} \\ &= \frac{2.3RT}{2F} \log K_{\text{IrOx}} + \frac{2.3RT}{2F} \log [\text{H}_2\text{O}_2] \\ &\quad - \frac{2.3RT}{F\alpha} \log \frac{I}{I_{\text{IrOx}}} \end{aligned} \quad (8)$$

where K_{IrOx} and I_{IrOx} are the reaction constant of the reaction shown in (4) and the exchange current, I_o , for the case of iridium oxide ($n = 1$), respectively.

It should be noted that the value of the exchange current density and α in (8) depend on the reaction between the gate material with hydrogen peroxide and the nature of the gate material. At a given gate material, the exchange current is influenced by the concentration of the species taking part in the redox reaction, which is hydrogen peroxide in this case [7]

$$I_{\text{IrOx}} = A[\text{H}_2\text{O}_2]^{1-\alpha} \quad (9)$$

where A is a constant. In the case of a reaction with iridium oxide, it was found that $\alpha = 0.14$ [8]. Substitution of (9) in (8) results in

$$\begin{aligned} V_T &= \frac{2.3RT}{2F} \left\{ \log K_{\text{IrOx}} + \frac{2(1-\alpha)}{\alpha} \log A \right\} \\ &\quad + \log [\text{H}_2\text{O}_2] + \frac{2(1-\alpha)}{\alpha} \log I[\text{H}_2\text{O}_2] \Big\} \\ &= \frac{2.3RT}{2F} \left\{ C + \log [\text{H}_2\text{O}_2] + \frac{2(1-\alpha)}{\alpha} \log I[\text{H}_2\text{O}_2] \right\}. \end{aligned} \quad (10)$$

Equation (10) is mathematically represented in Fig. 5. As can be seen, the same value of the threshold voltage is reached for lower values of the hydrogen peroxide concentration in case lower currents are applied. The sensitive range of the sensor is shifted depending on the value of the applied currents. The same yields for a higher value of C : lower values of the hydrogen peroxide can already give a certain value of the threshold voltage. Fig. 6 shows the measured dependence of the threshold voltage of the E MOSFET having an iridium oxide gate on the hydrogen peroxide concentration as a function of the applied current. When a reducing current of 25 nA is applied, the sensor is sensitive to hydrogen peroxide in a range from 100 μM to 1.5 mM. The high sensitivity of the sensor to hydrogen peroxide as shown in Fig. 6 can be explained by differentiating (10) with respect to $\log([\text{H}_2\text{O}_2])$

$$\frac{d(V_T)}{d\log([\text{H}_2\text{O}_2])} = \frac{2.3RT}{2F} + \frac{2.3RT}{F} \frac{1-\alpha}{\alpha}. \quad (11)$$

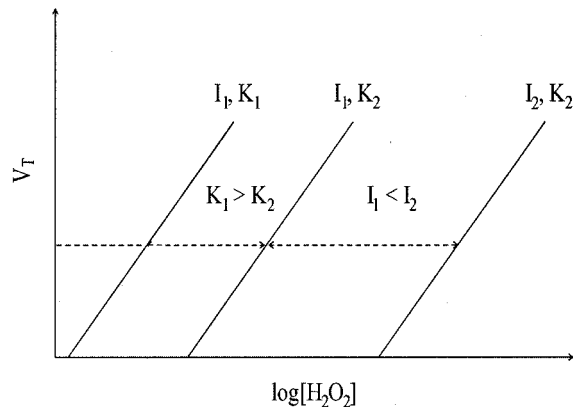


Fig. 5. Mathematical illustration of the relationship between the threshold voltage and the hydrogen peroxide concentration presented by (10) when the equilibrium constant K_i and the value of the applied current I_j are changed.

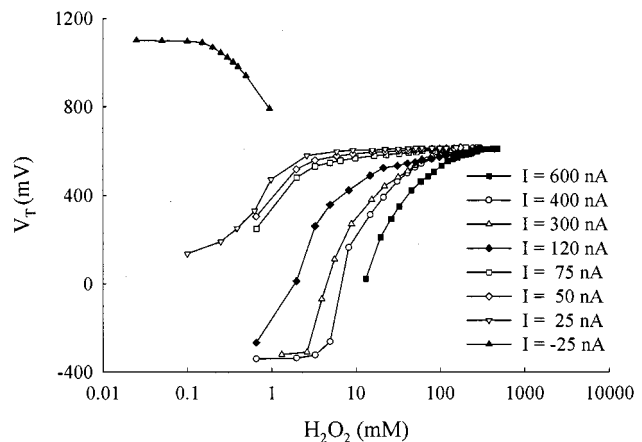


Fig. 6. The sensitivity and the sensitive range of the sensor based on the E MOSFET having an IrO_x gate depend on the external applied current densities.

This sensitivity can not be obtained by using a conventional potentiometric sensor. Analyzing (11), it shows that the first term of this equation is the same as a normal Nernstian slope of 28 mV/decade, which is typical for the conventional potentiometric hydrogen peroxide sensor. The second term of this equation, which is only appearing due to applying the external current and measuring V_T , gives the sensor the sensitivity of 600 mV/decade at the applied current of 120 nA, from which it can be calculated that $\alpha = 0.1$ in this particular case. According to (11), the sensitivity of the sensor is not influenced by the value of the applied current. It depends only on the value of α which reflects the nature of the gate material.

In addition, as seen in Fig. 6, the “sensitive window” of the sensor can be tuned by changing the value of the current. When the current density increases, the sensitive range of the sensor is shifted to a higher value of the hydrogen peroxide concentration. Moreover, it can be shown that, although the equilibrium constant of reaction (4) is brought into a constant C [see (10)], it still influences the detection limit of the sensor. The higher the value of the reaction constant of the reaction, the better the catalytic property of the gate material, the lower the detection limit of the sensor will be. This can be understood by considering

the fact that the ratio of oxidized to reduced iridium oxide, as present in (4) can only exist in a limited range.

Because of its properties, hydrogen peroxide can oxidize or reduce the gate material depending on its potential. A similar explanation can be given in the case where an external oxidizing current is applied. If the applied current is oxidizing, the reduction of the iridium oxide by the hydrogen peroxide can be presented as



In this case, the dissolved oxygen in the solution influences also V_T . However, considering the dissolved oxygen concentration to be constant due to equilibrium with oxygen in the air, the expression for V_T can be written as

$$V_T = -\frac{2.3RT}{2F} \log K'_{\text{IrOx}} - \frac{2.3RT}{2F} [\text{H}_2\text{O}_2] + \frac{2.3RT}{F\alpha} \frac{I}{I_{\text{IrOx}}} \quad (13)$$

where K'_{IrOx} is the equilibrium constant of the reaction shown in (12). One experimental curve for a case when an oxidizing current (-25 nA) is applied is also shown in Fig. 6. It can be seen that the sensitivities of the sensor in both cases when applying oxidizing or reducing current are identical. In practice, depending on the interfering species in the analyte, one can apply a suitable current (oxidizing or reducing) to avoid the influence of the interfering species on the electrode reaction, to obtain a good selectivity. The current should shift the present equilibrium to a situation that sensitivity for the measured hydrogen peroxide is higher than for the interferent. Another advantage of the iridium oxide gate is its physical and chemical stability. The sensor can operate across a wide range of temperatures and pH. The disadvantage of the sensor is its relatively poor detection limit due to the relative poor catalytic property of iridium oxide.

B. H_2O_2 Sensor Based on Prussian Blue

Prussian Blue is mentioned in literature related to hydrogen peroxide determination as “artificial peroxidase” due to its high catalytic properties to hydrogen peroxide in the presence of oxygen. It is an inorganic polycrystal of ferric ferrocyanide, which can be used for sensing of hydrogen peroxide at around 0 V. In literature, an amperometric sensor based on PB can detect hydrogen peroxide in the range from $0.2 \mu\text{M}$ to $100 \mu\text{M}$ (microM) [9]. The cyclic voltammogram of electrochemically deposited PB shows fine reversible redox peaks which correspond to the redox process of $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{1-}/\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]^{2-}$ (see Fig. 7). When the applied potential was swept from -0.1 V to 0.5 V, the color of the film changed from white (PW) to blue (PB) due to the electron transfer from a ground state $\text{Fe}(\text{II})\text{Fe}(\text{II})$ to an excited state $\text{Fe}(\text{II})\text{Fe}(\text{II})$, i.e., a change in the oxidation ratio of the PB.

The operation of the hydrogen peroxide sensor, based on PB oxidation by hydrogen peroxide, is described in (14).

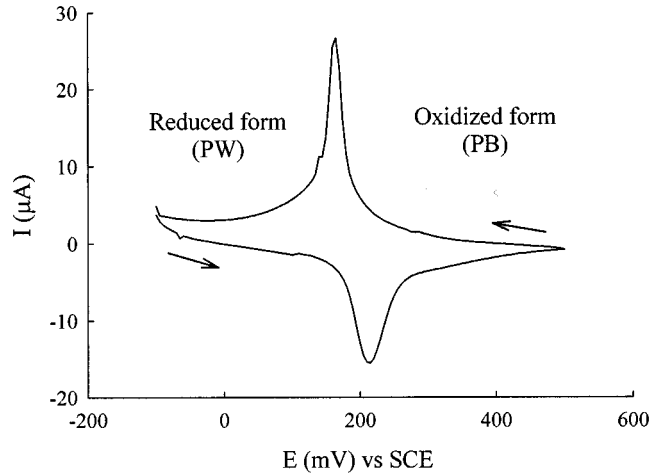
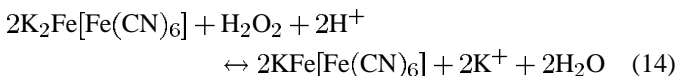


Fig. 7. Cyclic voltammogram of a Prussian Blue film at a sweep rate of 100 mV/s in phosphate buffer, pH 6.

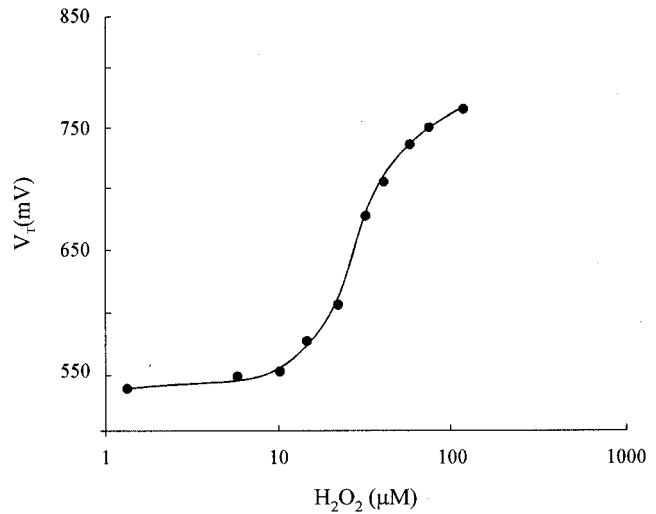


Fig. 8. Threshold voltage of the E^{MOSFET} having a Prussian Blue gate as a function of H_2O_2 concentration in phosphate buffer, pH 6, when a reducing current of 50 nA is applied.

Assuming the concentration of potassium ions as well as the pH to be constant, similarly to the case of iridium oxide, the change in the ox/red ratio of PB depends on hydrogen peroxide concentration and an external reducing current:

$$V_T = \frac{2.3RT}{2F} \log K_{\text{PB}} + \frac{2.3RT}{2F} \log [\text{H}_2\text{O}_2] - \frac{2.3RT}{F\alpha} \log \frac{I}{I_{\text{PB}}} \quad (15)$$

where K_{PB} represents the equilibrium constant of (14). The sensitivity of the hydrogen peroxide sensor, based on the E^{MOSFET} having a Prussian Blue gate as a function of hydrogen peroxide concentration when a reducing current of 50 nA is applied, is shown in Fig. 8.

In comparison with iridium oxide, as seen in Fig. 6, the sensitivity to hydrogen peroxide of the sensor based on PB is less and the sensitivity range of the sensor is not as large as shown in the case of iridium oxide. However, Prussian Blue shows better catalytic behavior to hydrogen peroxide than

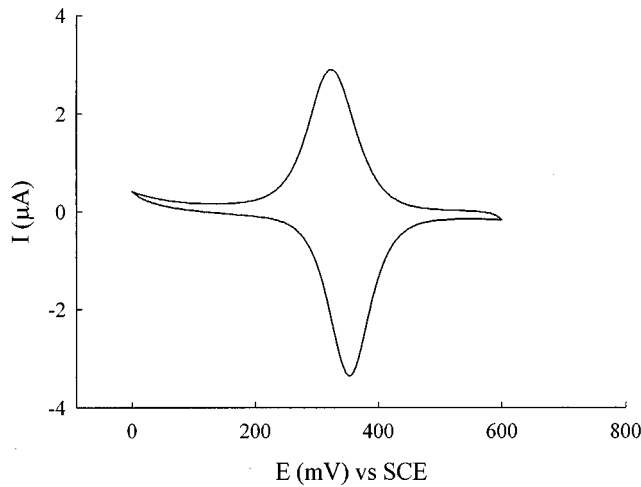


Fig. 9. Cyclic voltammogram of the Os-polyvinylpyridine containing HRP in phosphate buffer, pH 7.1.

iridium oxide ($K_{PB} > K_{IrOx}$). At the applied reducing current of 50 nA, the detection limit of the sensor is estimated to be about 10 μ M (microM). In contrast to the previous hydrogen peroxide sensors, the sensor based on PB works only in weak acidic media (pH \sim 4–6), which stabilizes PB. The stability of PB might be improved by growing more regular crystals during deposition.

C. H_2O_2 Sensor Based on Os-Polyvinylpyridine (Os-PVP) Containing Horseradish Peroxidase (HRP)

In order to improve the selectivity and detection limit of the hydrogen peroxide sensor, we should apply material which has a higher catalytic property to hydrogen peroxide than those shown above, such as an enzyme. The catalyst can directly be used as the gate material or it can be immobilized into a gate membrane material. For this purpose, we have chosen horseradish peroxidase (HRP) because it is known as an enzyme which can selectively catalyze the reduction of hydrogen peroxide [10]. HRP can easily be immobilized in the cross-linked redox polymer Os PVP, which is a nondiffusional mediator. This polymer contains Os centers bounded in long polymer chains, which results in a direct electrical communication between the enzyme and the electrode surface. At the same time, the polymer prevents leaching out of the enzyme and simultaneously improves the lifetime of the sensor [11]. Moreover, the Os centers in the polymer can be changed from the reduced (Os^{2+}) to the oxidized state (Os^{3+}) depending on their redox reaction with the enzyme. The cyclic voltammogram of Os^{2+}/Os^{3+} couple in phosphate buffer is shown in Fig. 9, where no reduction or oxidation of the enzyme can be seen.

Therefore, the mechanism of the reduction of hydrogen peroxide (see Fig. 10) by the redox polymer containing HRP can be interpreted as follows

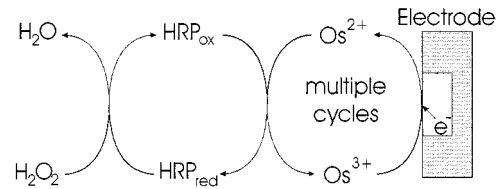
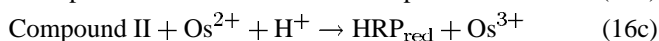
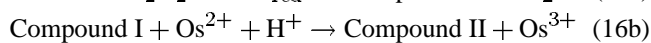
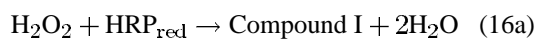


Fig. 10. Electrocatalytic reduction of H_2O_2 on an Os-polyvinylpyridine containing HRP electrode.

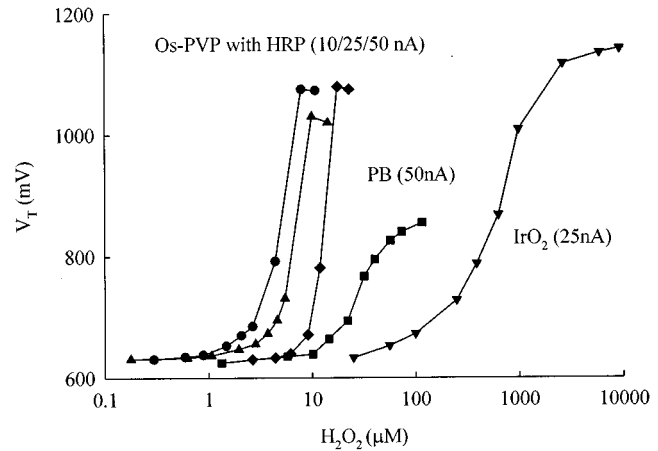


Fig. 11. Dependence of the threshold voltage on the H_2O_2 concentration for Os-PVP with HRP and for comparison for PB (Fig. 8) and IrO_x (Fig. 6) at different values of an applied reducing current.

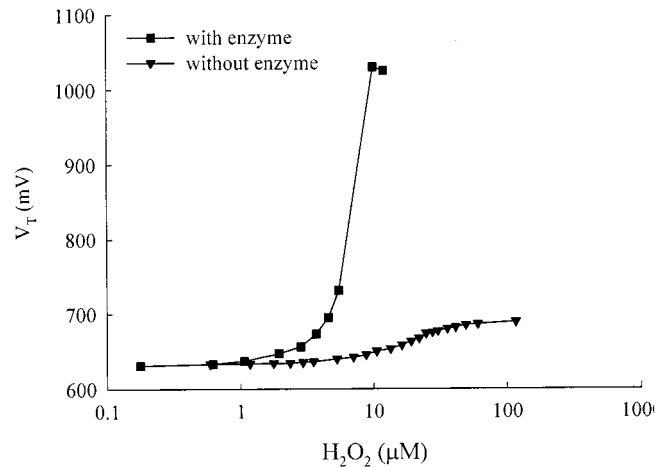
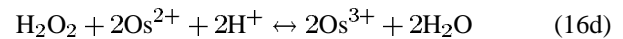


Fig. 12. Sensitivity of the sensor depends on the catalytic property of the gate material in phosphate buffer, pH 7, when a reducing current of 25 nA is applied.



where

- HRP_{red} ferric form of the enzyme (Fe^{2+});
- Compound I oxidized form of the enzyme (Fe^{4+});
- Compound II intermediate form of the enzyme (Fe^{3+}).

When a small amount of the hydrogen peroxide solution is added to the buffer solution, the oxidized HRP (compound I) is extremely rapidly formed ($k_1 = 9.10^6 \text{ M}^{-1}\text{s}^{-1}$) and is dissociated to HRP_{red} and H_2O_2 much more slowly (k_{-1} about $3 \text{ M}^{-1}\text{s}^{-1}$) [12].

TABLE I
SOME CHARACTERISTICS OF THE POSSIBLE GATE MATERIALS.

Material	Catalytic properties	Stability	Sensitivity (mV/dec)	pH range	H ₂ O ₂ range (M)
Iridium oxide	bad	good	400	3.5 - 9	10 ⁻⁴ - 10 ⁻¹
Prussian Blue	medium	bad	290	4.5 - 6	10 ⁻⁵ - 10 ⁻³
Os-PVP containing peroxidase	high	bad	700	6.5 - 7.5	10 ⁻⁷ - 10 ⁻⁵

As explained above, the threshold voltage V_T , of the E_{MOSFET} having the Os-polyvinylpyridine containing HRP gate, depends on the ox/red ratio of the polymer $[\text{Os}^{3+}]/[\text{Os}^{2+}]$

$$V_T = \frac{2.3RT}{F} \log \frac{(\gamma_{\text{Os}^{3+}})[\text{Os}^{3+}]}{(\gamma_{\text{Os}^{2+}})[\text{Os}^{2+}]} \quad (17)$$

where γ is the activity coefficient and $[\text{Os}^{n+}]$ is the concentration of the Os^{n+} centers in the polymer, respectively.

Using reaction (16d) with constant pH and when a reducing current is applied, the V_T which reflects the osmium oxidation state, is described by

$$V_T = \frac{2.3RT}{2F} \log K_{\text{OsPVP}} + \frac{2.3RT}{2F} \log [\text{H}_2\text{O}_2] - \frac{2.3RT}{F\alpha} \log \frac{I}{I_{\text{OsPVP}}} \quad (18)$$

where K_{OsPVP} is the equilibrium constant of the reaction shown in (16d).

The dependence of V_T on the hydrogen peroxide concentration of the sensor using the enzyme is shown in Fig. 11. This is different from the previous results: for the sensor based on the enzyme, the value of the applied current, which shifts the detection limit of the sensor, should be much smaller due to the high reactivity of the enzyme. For the same reason, the E_{MOSFET} having the Os-PVP containing the peroxidase gate has a higher sensitivity and a lower detection limit to hydrogen peroxide ($K_{\text{Os-PVP}} > K_{\text{PB}} > K_{\text{IrOx}}$). The enzyme is an excellent catalyst. Thus, the sensor operates in a quite low range of the hydrogen peroxide concentration. On the other hand, the sensitive range of the sensor is not large due to very high catalytic property of the enzyme. In Fig. 12, the dependence of V_T on the hydrogen peroxide concentration of the sensor using pure Os PVP (without enzyme) was plotted to clarify the influence of the enzyme on the sensitivity and the detection limit of the sensor [13]. When the enzyme concentration in the gate membrane decreases, the sensitivity and detection limit of the sensor decrease while the sensitive range of the sensor is enlarged.

The disadvantage of the sensor with the enzyme is its stability in storage. It is not always convenient because the sensor should be kept at 4 °C. Despite that, Os-PVP is a promising candidate

for developing a highly sensitive and selective hydrogen peroxide sensor.

V. CONCLUSION

We have shown new possibilities to determine hydrogen peroxide concentration by using an E_{MOSFET} having an electroactive gate material without using a reference electrode. The working principle of the sensor is based on measuring the change in the work function of the gate material, which is electronically conducting during its redox reaction with hydrogen peroxide. The higher the catalytic property of the gate material to the hydrogen peroxide, the lower the detection limit of the sensor will be. The addition of an auxiliary direct current applied between the gate of the E_{MOSFET} and the solution is necessary because it accelerates the equilibrium reaction and, with that, increases the sensitivity of the sensor. By changing the applied current density, the sensitive range of the sensor can be enlarged and tuned from a low to a high range of concentration of species to be measured. All materials used have shown sensitive properties to H_2O_2 , which are summarized in Table I, including some other characteristics. As can be seen from this table, all materials have specific properties that makes a wide range of the sensor application in general uses possible. We can choose a suitable material and a value of the applied current for a specific application (for example the range of the hydrogen peroxide concentration to be detected, pH, expected interference, etc.) to get a sensor with required properties.

Note that all materials investigated in this paper are based on modulation of the ox/red ratio of the gate material by hydrogen peroxide. Basically, this type of redox sensors will always have a lack in selectivity because all analytes with reducing or oxidizing properties will have effects. Use of specific catalysts may improve the selectivity as shown with the applied enzyme, but this will never result in 100% selectivity. Another possibility is the adding of a NAFION membrane to prevent interference, such as ascorbic acid [14]. It may also be useful to investigate nonredox materials which are sensitive for hydrogen peroxide in the sense that hydrogen peroxide will change their work function (electrochemical potential) and thus the V_T of

the E^+ MOSFET is modulated by an exchange reaction with hydrogen peroxide.

From the literature [15], it is known that the perovskite oxide ($A_{1-x}A'_xBO_{3-\delta}$ where A is lanthanide element, A' is alkaline metal and B is first row transition metal) can be used as material for a hydrogen peroxide sensor due to its large surface area and the presence of a high oxygen vacancy concentration. These oxygen vacancies can be seen as a dopant in the perovskite oxide. Depending on values of x and δ (delta), which influence the concentration of oxygen vacancies in the oxide crystal, the perovskite oxide shows the possibility to decompose hydrogen peroxide and thus the doping level of the perovskite oxide is changed depending on the exchange reaction with hydrogen peroxide. It demonstrates the possibility of measuring hydrogen peroxide by monitoring the change in the doping level, i.e., the concentration of the oxygen vacancies in the perovskite, using the E^+ MOSFET.

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